

Synthesis and *ab-initio* XRPD structure of group 12 imidazolato polymers

Norberto Masciocchi,^{*a} G. Attilio Ardizzoia,^{*a} Stefano Brenna,^a Fulvio Castelli,^a Simona Galli,^a Angelo Maspero^a and Angelo Sironi^b

^a Dipartimento di Scienze Chimiche, Fisiche e Matematiche, Università dell'Insubria, via Valleggio 11, 22100 Como, Italy. E-mail: norberto.masciocchi@uninsubria.it; Fax: 39-031-2386119;

Tel: 39-031-326227

^b Dipartimento di Chimica Strutturale e Stereochimica Inorganica and CNR-ISTM, Università di Milano, via Venezian 21, 20133 Milano, Italy

Received (in Cambridge, UK) 13th March 2003, Accepted 18th June 2003

First published as an Advance Article on the web 2nd July 2003

Two new 3D homoleptic binary imidazolates, Cd(im)₂ and Hg(im)₂ (Him = imidazole), as well as [Hg(im)]NO₃, containing 1D polycations of [Hg(im)]_nⁿ⁺ formulation, have been prepared and characterized by *ab-initio* XRPD methods.

Polyazaheteroaromatic ligands such as pyrazole (Hpz), imidazole (Him) and, more recently, 2-hydroxypyrimidine (2-Hpymo), have been extensively employed, in their deprotonated forms, in building a large variety of polynuclear complexes and polymeric systems.¹ Their most common coordination fashion is the μ_2 - $\eta^1(\text{N})$: $\eta^1(\text{N})$ -*exo*-bidentate one, although (for heavily substituted heterocycles) more exotic stereochemistries are also known.²

A number of homoleptic metal azolates have been recently synthesized and shown to possess interesting properties, such as high thermal stability,³ magnetic hysteresis,⁴ luminescence,⁵ as well as anticorrosive,⁶ sorption,⁷ protein staining⁸ and antimicrobial activity.⁹ Despite their simple formulation, their rigid nature and the highly predictable (local) coordination geometry, metal imidazolates have afforded a variety of structural types, ranging from one-dimensional chains, to 2D and 3D polymers, showing, occasionally, crystalline polymorphic species with distinct topologies and spectroscopic features.¹⁰

Two complex tetragonal, not isostructural, crystalline phases [Zn(im)₂ and Co(im)₂] have long since been known;¹¹ more recently, the Ag(i)¹² and the pentamorphic Cu(ii)¹⁰ polymers have been reported, while Cu(im), prepared by ourselves¹³ and others¹⁴ in the past, still awaits a full structural characterization. Analogously, our recent report on Ni(im)₂¹⁵ has shown that only amorphous samples or complex polyphasic mixtures can be prepared, thus hampering satisfactory structural studies.

When Et₃N was added to an acetonitrile solution of Hg(NO₃)₂ and imidazole (Hg/Him ratio = $\frac{1}{2}$) the sudden formation, as a white precipitate, of the mixed ligand [Hg(im)(NO₃)] species [1] was observed. Any attempt to obtain by this route the binary Hg(im)₂ derivative failed, complex 1 being persistently recovered. On the contrary, highly crystalline Hg(im)₂ [2] was obtained from water solutions of Hg(CH₃COO)₂ and Him, employing aqueous NH₃ as the deprotonating agent. With a similar approach, Zn(im)₂ and Cd(im)₂¹⁶ [3] derivatives were obtained, as highly insoluble powders, from the corresponding perchlorate salts in aqueous medium. We proved by X-ray powder diffraction (XRPD) that the former contains a pure crystalline phase identical to that reported in ref. 11b, characterised thanks to the occasional availability of a suitable single crystal.

For the remaining three phases (1, 2 and 3), all structural (and spectroscopic[†]) information had to be gathered from polycrystalline samples only, taking advantage of the *ab-initio* XRPD methodology developed in the recent past, by others and us, in the realm of coordination polymers.

Our diffraction studies[‡] revealed that 2 and 3 are isomorphous (orthorhombic *Pbca*) and share nearly identical

lattice parameters. They contain a crystallographically unique metal ion (in general position) and two crystallographically independent imidazolato ligands, bridging, in their common *N*, *N'*-*exo*-bidentate mode, metal atoms which are 6.34–6.48 and 6.37–6.43 Å apart (2 and 3, respectively). The coordination geometry about the M(ii) ions is pseudo-tetrahedral (Cd–N 2.17–2.24 Å, N–Cd–N 99.8–117.5°; Hg–N 2.17–2.32 Å, N–Hg–N 98.2–117.6°). While expected for Cd(ii), this is “exceptional” for Hg(ii), which, in the pyrazolate analogue,¹⁷ had been found to be linearly coordinated by two monodentate pz moieties.

The supramolecular arrangement of 2 and 3 needs a further comment; while a 3D diamondoid network is not totally unexpected for tetrahedral centres and bidentate spacers, its twofold interpenetration (see Figure 1) is rather surprising: since imidazolates are not easily assimilated to rods or spacers of elongated (nearly cylindrical) shape, it is therefore amazing that such short intermetallic contacts are compatible with interpenetration. *Inter alia*, 2 and 3 are the smallest coordination polymers possessing this peculiar feature [apart from *inorganic* Zn(CN)₂].

Interestingly, this topological occurrence cannot be achieved if metals of small(er) ionic radii are employed (Zn,^{11b} Co^{11a} and Cu¹⁰ bis-imidazolates). Differently, Cd (but *not* Hg,¹⁷ due to its peculiar stereochemical requirements) and first-row transition metals (Fe, Co, Cu and Zn)¹⁵ tetrahedral bis-pyrazolates, for which interpenetration is not possible, are found to be isomorphous, although not completely miscible.

At variance from pyrazolates, the structures of known M(im)₂ species are very different in connectivity, dimensionality and topology. This agrees with the inaccessibility of M–(im)_n–M bridges for *n* > 1, which leaves metal imidazolates with just the flexible M–(im)–M structural motif, *always* arranged

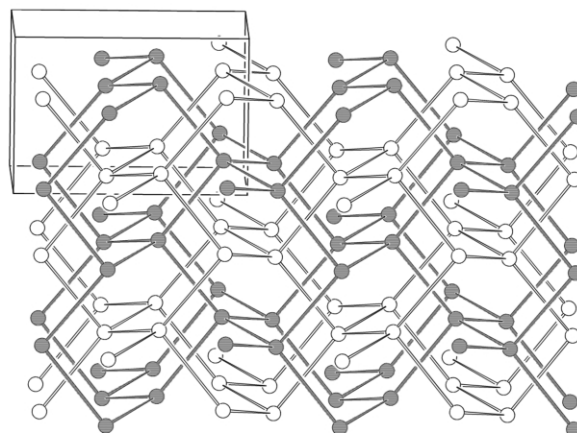


Fig. 1 Schematic drawing of the crystal packing of 2, highlighting the two interpenetrated diamondoid networks (black and white).

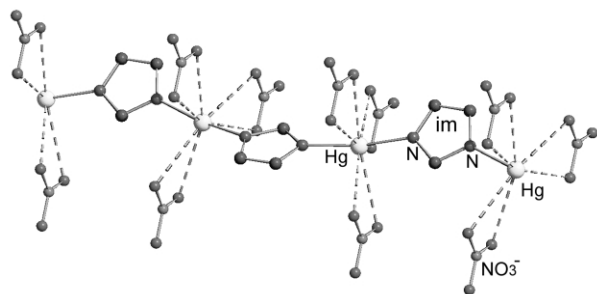


Fig. 2 Schematic drawing of a portion of the $[\text{Hg}(\text{im})]_n^{n+}$ chain, running parallel to c and surrounded by loosely interacting (dashed lines) nitrate ions. Hydrogen atoms omitted for clarity.

within 2D or 3D networks. In contrast, pyrazolates assemble as rigid (collinear) $\text{M}-(\text{pz})_n-\text{M}$ fragments within 1D polymers.¹⁵

The crystals of the mixed anion phase **1** are non-centrosymmetric, $P-62c$: metal ions and imidazoles lie in special positions (twofold axes), while two crystallographically independent NO_3^- anions (of different site symmetries) occupy the voids near the origin and on threefold axes at $(2/3, 1/3, z)$. That species **1** is acentric was also confirmed by SHG measurements, its activity being 0.1 times that of urea, **2** and **3** giving, under the same experimental conditions (Kurtz–Perry powder technique, incident wavelength 1907 nm), null signals.

Compound **1** contains linearly coordinated $\text{Hg}(\text{II})$ ions, bridged by N,N' -imidazoles with $\text{Hg}-\text{N}$ values of 2.03 Å, forming 1D $[\text{Hg}(\text{im})]_n^{n+}$ chains running parallel to c ($\text{Hg}\cdots\text{Hg}$ 6.06 Å, see Figure 2). The dihedral angle between adjacent imidazoles is 150° , thus significantly different from that of the $\text{Ag}(\text{im})$ species,¹² where nearly coplanar imidazoles form a wavy polymer.

Non-negligible $\text{Hg}\cdots\text{O}$ contacts (in the 2.75–2.94 Å range) are present in the plane normal to the $\text{Hg}-\text{N}$ vectors, possibly favouring the sudden precipitation of **1**, as if it were a solid with extensive three-dimensional nature. A similar polycation, embedded in a nitrate matrix, has been observed in $[\text{Hg}(\text{pz})]\text{NO}_3$,¹⁷ which separated as an insoluble species in the attempt of preparing the homoleptic mercury pyrazolate on starting from $\text{Hg}(\text{NO}_3)_2$.

The systems reported above have not (yet) demonstrated the presence of polymorphs: all preparations (differing in temperature, concentrations or solvents) tackled in our laboratory

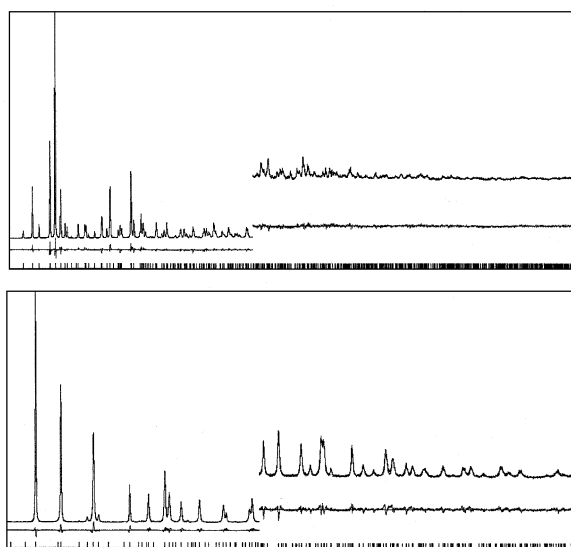


Fig. 3 Rietveld refinement plots for **1** (bottom) and **2** in the $10\text{--}100^\circ$ range with difference plots and peak markers at the bottom. The section above 50° has been magnified (5x).

gave pure crystalline phases with no traces of contamination. This is somewhat surprising, particularly after it has been demonstrated that polymorphism of analogous species is not a rare occurrence,¹⁰ which, when not annoying, can be positively used to better understand the underlying crystal chemistry and the nature of subtle stabilizing effects.

The University of Insubria ('Progetto di Ateneo Sistemi Poliazotati'), the Chamber of Commerce of Como and ICDD are acknowledged for funding. The courtesy of Dr E. Cariati for performing SHG measurements is also acknowledged.

Notes and references

† IR spectral data (nujol mulls, cm^{-1}): **1**; 3052 (m), 1343 (s), 1192 (w), 1112 (m), 1095 (s), 827 (w), [758, 723, 712] (sh, w); **2**, 1283 (w), 1244 (w), 1163 (w), 1108 (m), 1083 (s), 937 (m), [840, 832, 823, 812], (sh, w), [752, 743, 722], (sh, w), 656 (m); **3**, 1277 (w), 1244 (w), 1163 (w), 1112 (m), 1087 (s), 943 (m), [840, 834, 827, 818] (sh, w), [756, 746, 722] (sh, w), 662 (m). Elemental analyses: **1**, Calcd. for $\text{C}_3\text{H}_3\text{HgN}_3\text{O}_3$: C 10.93, H 0.92, N 12.75; Found: C 11.28, H 0.79, N 13.17; **2**, Calcd. for $\text{C}_6\text{H}_6\text{HgN}_2$: C 21.53, H 1.81, N 16.74; Found: C 21.70, H 1.82, N 15.47; **3**, Calcd. for $\text{C}_6\text{H}_6\text{CdN}_2$: C 29.23, H 2.45, N 22.72; Found: C 29.48, H 2.31, N 21.93.

‡ Crystal data: $[\text{Hg}(\text{im})]\text{NO}_3$, **1**, $\text{C}_3\text{H}_3\text{HgN}_3\text{O}_3$, $M = 329.66$; hexagonal, $P-62c$, $a = 9.5488(2)$; $c = 12.1150(3)$ Å; $V = 956.1(1)$ Å³, $Z = 6$, $\mu = 43.0$ mm^{-1} ; $R_{\text{wp}} = 0.107$; $R_{\text{B}} = 0.039$; $\text{Hg}(\text{im})_2$, **2**, $\text{C}_6\text{H}_6\text{HgN}_4$, $M = 334.74$; orthorhombic, $Pbca$, $a = 14.5899(3)$; $b = 10.8076(2)$; $c = 9.8200(2)$ Å; $V = 1548.4(1)$ Å³, $Z = 8$, $\mu = 35.1$ mm^{-1} ; $R_{\text{wp}} = 0.097$; $R_{\text{B}} = 0.059$; $\text{Cd}(\text{im})_2$, **3**, $\text{C}_6\text{H}_6\text{CdN}_4$, $M = 246.55$; orthorhombic, $Pbca$, $a = 14.6045(5)$; $b = 10.7385(3)$; $c = 9.9229(4)$ Å; $V = 1556.2(1)$ Å³, $Z = 8$, $\mu = 22.0$ mm^{-1} ; $R_{\text{wp}} = 0.106$; $R_{\text{B}} = 0.057$; Bruker AXS D8 θ : θ diffractometer, graphite monochromatised $\text{Cu}-\text{K}\alpha$, ($\lambda = 1.5418$ Å); $10 < 2\theta < 105^\circ$ range, $\Delta 2\theta = 0.02^\circ$; indexing by TREOR;¹⁸ solution by simulated annealing and Rietveld refinement by TOPAS-R¹⁹ (see Figure 3). Imidazoles treated as rigid bodies. Preferred orientation correction on the (001), **1**, (010), **2** and **3**, poles. Anisotropic peak widths in **1**. CCDC reference numbers 205572–205574. See <http://www.rsc.org/suppdata/cc/b3/b302840b/> for crystallographic data in CIF or other electronic format.

- G. La Monica and G. A. Ardizzoia, *Prog. Inorg. Chem.*, 1997, **46**, 151; J. A. R. Navarro and B. Lippert, *Coord. Chem. Rev.*, 2001, **222**, 219.
- J. R. Perera, M. J. Heeg, H. B. Schlegel and C. H. Winter, *J. Am. Chem. Soc.*, 1999, **121**, 4536; J. R. Perera, M. J. Heeg and C. H. Winter, *Organomet.*, 2000, **19**, 5263 and references therein.
- N. Masciocchi, G. A. Ardizzoia, G. La Monica, A. Maspero and A. Sironi, *Eur. J. Inorg. Chem.*, 2000, 2507.
- J. Kröber, E. Codjovi, O. Kahn, F. Grolière and C. Jay, *J. Am. Chem. Soc.*, 1993, **115**, 9810; P. Gütllich, Y. Garcia and H. A. Goodwin, *Chem. Soc. Rev.*, 2000, **29**, 419.
- Y. Yang and R. G. Raptis, *Inorg. Chem.*, 2003, **42**, 261.
- W. N. Richmond, P. W. Faguy and S. C. Weibel, *J. Electroanal. Chem.*, 1998, **448**, 237.
- L. C. Tabares, J. A. R. Navarro and J. M. Salas, *J. Am. Chem. Soc.*, 2001, **123**, 383.
- L. Castellanos-Serra and E. Hardy, *Electrophoresis*, 2001, **22**, 864.
- K. Nomiya, K. Tsuda, T. Sudoh and M. Oda, *J. Inorg. Biochem.*, 1997, **68**, 39.
- N. Masciocchi, S. Bruni, E. Cariati, F. Cariati, S. Galli and A. Sironi, *Inorg. Chem.*, 2001, **40**, 5897.
- (a) M. Sturm, F. Brandel, D. Engel and W. Hoppe, *Acta Crystallogr.*, 1975, **B31**, 2369; (b) R. Lehnert and F. Seel, *Z. Anorg. Allg. Chem.*, 1980, **464**, 187.
- N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. La Monica, *J. Chem. Soc., Dalton Trans.*, 1995, 1671.
- PDF No. 52–2401, Powder Diffraction File, ICDD, Swarthmore, PA.
- A. V. Bukhtiarov, V. V. Mikheev and A. V. Lebedev, *J. Gen. Chem. USSR*, 1990, **60**, 1676; G. Cardini and M. Muniz-Miranda, *J. Phys. Chem. B*, 2002, **106**, 6875.
- N. Masciocchi, G. A. Ardizzoia, S. Brenna, G. La Monica, A. Maspero, S. Galli and A. Sironi, *Inorg. Chem.*, 2002, **41**, 6080 and references therein.
- M. Olczak-Kobza, *Thermochim. Acta*, 2001, **366**, 129.
- N. Masciocchi, G. A. Ardizzoia, G. La Monica, A. Maspero and A. Sironi, *Inorg. Chem.*, 1999, **38**, 3657.
- P. E. Werner, L. Eriksson and M. Westdahl, *J. Appl. Crystallogr.*, 1985, **18**, 367.
- A. Kern and A. Coelho, TOPAS-R, 2001, Bruker AXS GmbH, Karlsruhe, Germany.